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Thermal characterization of crude oils in the presence of limestone matrix by TGA-DTG-FTIR

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ABSTRACT

In present work oxidation of two heavy oils in limestone matrix was studied using simultaneous thermogravimetry (TGA), derivative thermogravimetry (DTG) and FTIR-spectroscopy techniques in the temperature range from 25 to 900 °C. Before the measurements, the composition and properties of crude oils and limestone were evaluated. Obtained TG and DTG curves shows four different reaction regions: low temperature oxidation (LTO), fuel deposition (FD), high temperature oxidation (HTO) and decomposition of limestone. LTO reactions were accompanied by evaporation of light hydrocarbons, which was confirmed by appearance of stretching vibration bands of C-H groups in FTIR-spectra of evolved gases. Formation of carbon dioxide was observed for all oxidation reaction regions according to spectroscopic data. At the same time, CO was formed only in HTO region for both studied crude oils. Despite the different composition two crude oils have practically the same reactions intervals and peak temperatures. However, crude oil with higher API-gravity has a greater mass loss at the LTO and evaporation regions. The conversion of heavier oil with higher content of asphaltenes is larger during the high-temperature oxidation step.

Three different kinetic models (Arrhenius, Coats & Redfern and Ingraham & Marrier) were used for analysis of TGA-DTG curves in LTO and HTO regions. Activation energy values of the crude oil samples were varied between 6.9–10.6 kJ/mol in low temperature oxidation and 91.8-.0–181.9 kJ/mol in high temperature oxidation regions. For two crude oils activation energies are similar in low temperature oxidation region. In high temperature oxidation region, crude oil with higher content of asphaltenes has larger activation energy.

1. Introduction

Crude oil is the most important energy and petrochemicals source, which consumption increases every year. Because of the substantial depletion of conventional light crude oil, heavy crude oils resources become a major feedstock for the petroleum industry. In-situ combustion (ISC) is one of the promising methods of heavy oil recovery. In accordance with ISC technology direct heat effect as a result of combustion processes reduces the oil viscosity by several orders of magnitude and induces partial upgrading of heavy oil. Combustion process is caused by the injection of air into the well. Preliminary tests have shown that the use of in-situ combustion technology can achieve the greatest performance of recovery rates compared with other methods for enhanced oil recovery. Heat generated directly inside the oil reservoir significantly reduces the heat loss and reduces power consumption compared with other thermal techniques. All these facts make in-situ combustion an attractive method to increase the efficiency of heavy oil production. However, the practical application of in-situ combustion technology has a number of problems induced by simultaneous combination of mass and heat transfer processes with a variety of homo- and heterogeneous reactions in porous media, which are difficult to control. Successful implementation of ISC technology on the field requires detailed laboratory studies of crude oil oxidation reactions and evaluation of kinetic parameters of these chemical processes.

Among different methods of studies of oxidation processes, thermal analysis and calorimetry techniques can be more useful for preliminary screening of ISC technology. These methods give fast and accurate information about the ignition temperature of crude oils, temperature intervals and kinetic parameters of oxidation regions. Also, they help to evaluate effect of different additives and oil and rock composition on the oxidation reactions. Application of thermal analysis techniques combined with structural methods like FTIR-spectroscopy, gas chromatography or mass-spectrometry allow to analyze the gaseous products and mechanisms of combustion process. Thermal analysis

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